

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :  
Tsutomu TAMURA, et al. : Docket No. 2356/15  
Serial No. 10/537,917 : Group Art Unit 1796  
Filed on November 28, 2006 : Examiner: Ana L. Woodward  
For: MATERIAL FOR FUEL-SYSTEM PART AND FUEL-SYSTEM PART  
COMPRISING THE SAME

DECLARATION UNDER 37 CFR §1.132

Honorable Commissioner of  
Patents,  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

Sirs:

I, Gaku MARUYAMA, citizen of Japan, sincerely declare;

That I graduated from University of Shizuoka, Faculty of  
Science and Engineering in March 1999;

That I have been employed by Toyo Boseki Kabushiki Kaisha  
since April 1999, and have been engaged in the research and  
development of polymers at said company;

That I am one of inventors of the above-identified patent  
application; and

That I conducted the following experiment to demonstrate  
the unexpected, superior effect of the material for a fuel  
system part of the present invention, that the material is  
superior in the relationship between the both properties of  
impact strength at a low temperature of -40°C and alcohol-  
containing gasoline barrier property, the results of which  
follow hereunder.

Experiment

**Test materials**

(A) polyamide resin

As the polyamide resin, the following (1) - (6) were

prepared. (6) was used as Comparative Example free of a meta-xylylenediamine component.

(1) poly-meta-xylylene adipamide obtained by polycondensation of meta-xylylenediamine and adipic acid (hereinafter to be also referred to as MXD-6);

Relative viscosity (96% sulfuric acid method) was 2.1, the amount of amino terminal group was 80 eq/ton and glass transition temperature was 88°C.

(2) copolymer obtained by polycondensation of 3 kinds of compounds of meta-xylylenediamine (100 mol), adipic acid (85 mol) and terephthalic acid (15 mol) (hereinafter to be also referred to as MXD-6T);

Relative viscosity was 2.1, amount of amino terminal group was 82 eq/ton, melting point was 225°C and glass transition temperature was 107°C.

(3) poly-meta-xylylene pimelamide obtained by polycondensation of equimolar of meta-xylylenediamine and pimelic acid (hereinafter to be also referred to as MXD-7);

Relative viscosity was 2.2, amino terminal amount was 71 eq/ton and glass transition temperature was 50°C.

(4A) copolymer obtained by polycondensation of 3 kinds of compounds of meta-xylylenediamine (100 mol), adipic acid (90 mol), and 1,4-cyclohexanedicarboxylic acid (10 mol) (hereinafter to be also referred to as MXD-6CHDA-10A);

Relative viscosity was 2.1, amount of amino terminal group was 78 eq/ton, melting point was 245°C and glass transition temperature was 97°C.

(4B) copolymer obtained by polycondensation of 3 kinds of compounds of meta-xylylenediamine (100 mol), adipic acid (90 mol) and 1,4-cyclohexanedicarboxylic acid (10 mol) (hereinafter to be also referred to as MXD-6CHDA-10B);

Relative viscosity was 2.5, amount of amino terminal group was 54 eq/ton, melting point was 245°C and glass transition temperature was 97°C.

(5A) copolymer obtained by polycondensation of 3 kinds of compounds of meta-xylylenediamine (100 mol), adipic acid (80 mol) and 1,4-cyclohexanedicarboxylic acid (20 mol) (hereinafter to be also referred to as MXD-6CHDA-20A);

Relative viscosity was 2.1, amount of amino terminal group was 80 eq/ton, melting point was 258°C and glass transition temperature was 108°C.

(5B) copolymer obtained by polycondensation of 3 kinds of compounds of meta-xylylenediamine (100 mol), adipic acid (80 mol) and 1,4-cyclohexanedicarboxylic acid (20 mol) (hereinafter to be also referred to as MXD-6CHDA-20B);

Relative viscosity was 2.5, amount of amino terminal group was 52 eq/ton, melting point was 258°C and glass transition temperature was 108°C.

(6) nylon 66 resin (nylon T-662 manufactured by Toyo Boseki Kabushiki Kaisha);

Relative viscosity was 2.2, amino terminal amount was 82 eq/ton and glass transition temperature was 97°C.

The glass transition temperature was adjusted by controlling the temperature and time of polymerization of polyamide resin. In addition, terminal group amount was adjusted by adding a small amount of cyclohexylamine, which is a monofunctional amine, or acetic acid, which is a monofunctional carboxylic acid, to the polymerization starting material.

(B) resin having lower glass transition temperature than polyamide resin (A)

As resin (B), the following (i) - (iv) were used. (iv) was used as Comparative Example free of a functional group capable of reacting with polyamide resin.

(i) Maleic anhydride (0.8 part by weight, reagent special GR, manufactured by Nacalai Tesque) and organic peroxide (0.1 part by weight, percumyl DF manufactured by NOF Corporation) were added to linear medium density polyethylene resin (L-MDPE, 100

parts by weight, Neozex (trademark) 2015M manufactured by Mitsui Chemical) and the mixture was kneaded in a twin-screw extruder at a cylinder temperature of 210°C. The obtained modified L-MDPE was used. This resin had a glass transition temperature of -45°C and a melting point (DSC method) of 122°C.

(ii) Ethylene/butene copolymer (MI was 1.8, specific gravity was 0.87) modified with maleic anhydride (0.4 wt%) was used. This resin had a glass transition temperature of -59°C and a melting point (DSC method) of 55°C.

(iii) Ethylene/butene/styrene copolymer (MI was 2.4, specific gravity was 0.85) modified with maleic anhydride (1.4 wt%) was used. This copolymer showed an ethylene/butene/styrene molar ratio of 70/28/2. This resin had a glass transition temperature of -63°C and a melting point (DSC method) of 95°C.

(iv) Unmodified ethylene/butene copolymer (MI was 0.5, specific gravity was 0.86) was used. This resin was free of a functional group capable of reacting with a polyamide resin. This resin had a glass transition temperature of -60°C and a melting point (DSC method) of 54°C.

The glass transition temperature (T<sub>g</sub>) and melting point (T<sub>m</sub>) of each resin were determined according to JIS K 7121 based on the DSC measurement under the following conditions.  
(DSC measurement conditions)

apparatus: DSC3100 manufactured by Mac Science

pan: aluminum pan (non-airtight type)

sample weight: 10 mg

temperature rise start temperature: -150°C

temperature rise rate: 10°C/min

atmosphere: argon

These resins were measured in the amounts shown in Tables 1 - 6 and melt kneaded in a twin-screw extruder at a cylinder temperature 270°C, screw rotation speed 150 rpm. The composition (material) obtained using kneading was formed into various samples using an injection molding machine at a

cylinder temperature of 280°C and a metal mold temperature of 40°C, and subjected to the following evaluation.

### **Experimental method**

(determination of tensile property)

The tensile property was determined according to ASTM D-638, wherein the measurement atmosphere temperature was 23°C.  
(measurement of izod impact strength with notch)

The izod impact strength with notch was measured according to ASTM D-638 using a 4 mm thick sample. The measurement atmosphere temperature was -40°C.

(determination of permeability of alcohol-containing gasoline solution)

The permeability of the alcohol-containing gasoline solution was calculated from weight changes by a cup method according to JIS-Z0208. The specific procedures and alcohol-containing gasoline solution to be used for determining the permeability are as mentioned above. The formed part (measurement object) was a molded disc obtained by cutting one surface of an injection molded product (100 mm × 100 mm × thickness 1 mm) in a thickness of 0.5 mm. A lower permeability means superiority in alcohol-containing gasoline barrier property.

(observation of morphology structure)

Each resin composition was observed using a JEM2010 transmission electron microscope manufactured by JEOL. Ltd. The observation sample was prepared by cutting out a sample from the center of a sample having the same shape as the sample used for the above-mentioned tensile property, producing a frozen section of a surface perpendicular to the resin flow direction, coloring the section in RuO<sub>4</sub> vapor for 30 min and further subjecting the section to carbon vapor deposition. TEM observation was performed using a JEM2010 transmission electron

microscope manufactured by JEOL. Ltd. at an accelerating voltage of 200 kV and direct magnification  $\times 5000$  and photographed. Then, the obtained photograph was applied to an image analyzer to determine an area average particle diameter of about 100 domains. When the observed images of the domains are elliptical, this analyzer takes a diameter converted to that of a circle as a particle diameter.

## Results

The compositions and evaluation results of respective samples are shown in Tables 1 - 6 and Figure 1.

In the Tables, the numerical values in the column of composition are in parts by weight.

In the Tables, the "NB" under the item of "Izod impact strength with notch" refers to "non-break", which means being not broken, and the presence of high impact strength.

In the Tables, the "A" under the item of "morphology structure" means a structure wherein the matrix component is a polyamide resin and the domain component is a polyolefin resin, "B" means a structure wherein the matrix component is a polyolefin resin and the domain component is a polyamide resin, and "homogeneous" means that the both resins are homogenized and the matrix and domain cannot be identified.

In Figure 1, each plot shows the relationship between the measurement value of [Izod impact strength (J/m) at  $-40^{\circ}\text{C}$ ] (Izod Impact in Figure 1), and that of [alcohol-containing gasoline barrier property] (Permeability in Figure 1) appearing in the Examples and Comparative Examples of Tables 1-6. In Figure 1, the numeral values in the parenthesis show the amount (%) of resin (B). The white plots show the Examples of the present invention and the gray plots are those outside the scope of the present invention.

Table 1

		Ex. 1	Ex. 4	Ex. 5
Composition	(1)MXD-6			
	(2)MXD-6T	100	100	100
	(3)MXD-7			
	(4A)MXD-6CHDA-10A			
	(4B)MXD-6CHDA-10B			
	(5A)MXD-6CHDA-20A			
	(5B)MXD-6CHDA-20B			
	(6)nylon 66			
	(i)modified L-MDPE			7.7
	(ii)modified copolymer	54	38	38
Properties	(iii)modified copolymer			
	(iv)unmodified copolymer		15	7.7
	tensile strength (MPa)	35	37	40
	tensile elongation (%)	>160	>160	>160
	tensile elastic modulus (GPa)	1.6	1.6	1.8
	izod impact strength (J/m) at -40°C	680 - NB	625	450
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	4.0	6.8	3.5
	morphology structure	A	A	A
	average particle diameter (μm) of domain	0.8	0.8	0.7

Table 2

		Ex. 6	Ex. 9	Ex. 10
Composition	(1)MXD-6			
	(2)MXD-6T	100		
	(3)MXD-7			
	(4A)MXD-6CHDA-10A		100	
	(4B)MXD-6CHDA-10B			100
	(5A)MXD-6CHDA-20A			
	(5B)MXD-6CHDA-20B			
	(6)nylon 66			
	(i) modified L-DPE			
	(ii) modified copolymer	43	43	43
Properties	(iii) modified copolymer			
	(iv) unmodified copolymer			
	tensile strength (MPa)	43	43	42
	tensile elongation (%)	>160	>160	>160
	tensile elastic modulus (GPa)	1.9	1.8	1.7
	izod impact strength (J/m) at -40°C	290	420 - NB	450 - NB
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	0.35	0.45	0.25
	morphology structure	A	A	A
	average particle diameter (μm) of domain	0.8	0.8	0.7

Table 3

		Ex. 11	Ex. 12	Ex. 13
Composition	(1)MXD-6			
	(2)MXD-6T			
	(3)MXD-7			
	(4A)MXD-6CHDA-10A			
	(4B)MXD-6CHDA-10B	100		
	(5A)MXD-6CHDA-20A		100	
	(5B)MXD-6CHDA-20B			100
	(6)nylon 66			
	(i)modified L-MDPE			
	(ii)modified copolymer		43	43
Properties	(iii)modified copolymer	43		
	(iv)unmodified copolymer			
	tensile strength (MPa)	42	43	43
	tensile elongation (%)	>160	>160	>160
	tensile elastic modulus (GPa)	1.7	1.8	1.7
	ized impact strength (J/m) at -40°C	450 - NB	420 - NB	450 - NB
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	0.08	0.35	0.15
	morphology structure	A	A	A
	average particle diameter (μm) of domain	0.5	0.8	0.6

Table 4

		Comp. Ex 1	Comp.Ex. 2	Comp. Ex 3
Composition	(1)MXD-6	100		100
	(2)MXD-6T			
	(3)MXD-7			
	(4A)MXD-6CHDA-10A			
	(4B)MXD-6CHDA-10B			
	(5A)MXD-6CHDA-20A			
	(5B)MXD-6CHDA-20B			
	(6)nylon 66		100	
	(i)modified L-MDPE			
	(ii)modified copolymer			150
Properties	(iii)modified copolymer			
	(iv)unmodified copolymer			
	tensile strength (MPa)	95	75	8
	tensile elongation (%)	60	120	>160
	tensile elastic modulus (GPa)	3.6	2.2	0.3
	ized impact strength (J/m) at -40°C	30	45	NB
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	0.06	450	680
	morphology structure	homogeneou	homogeneou	B
	average particle diameter (μm) of domain	-	-	-

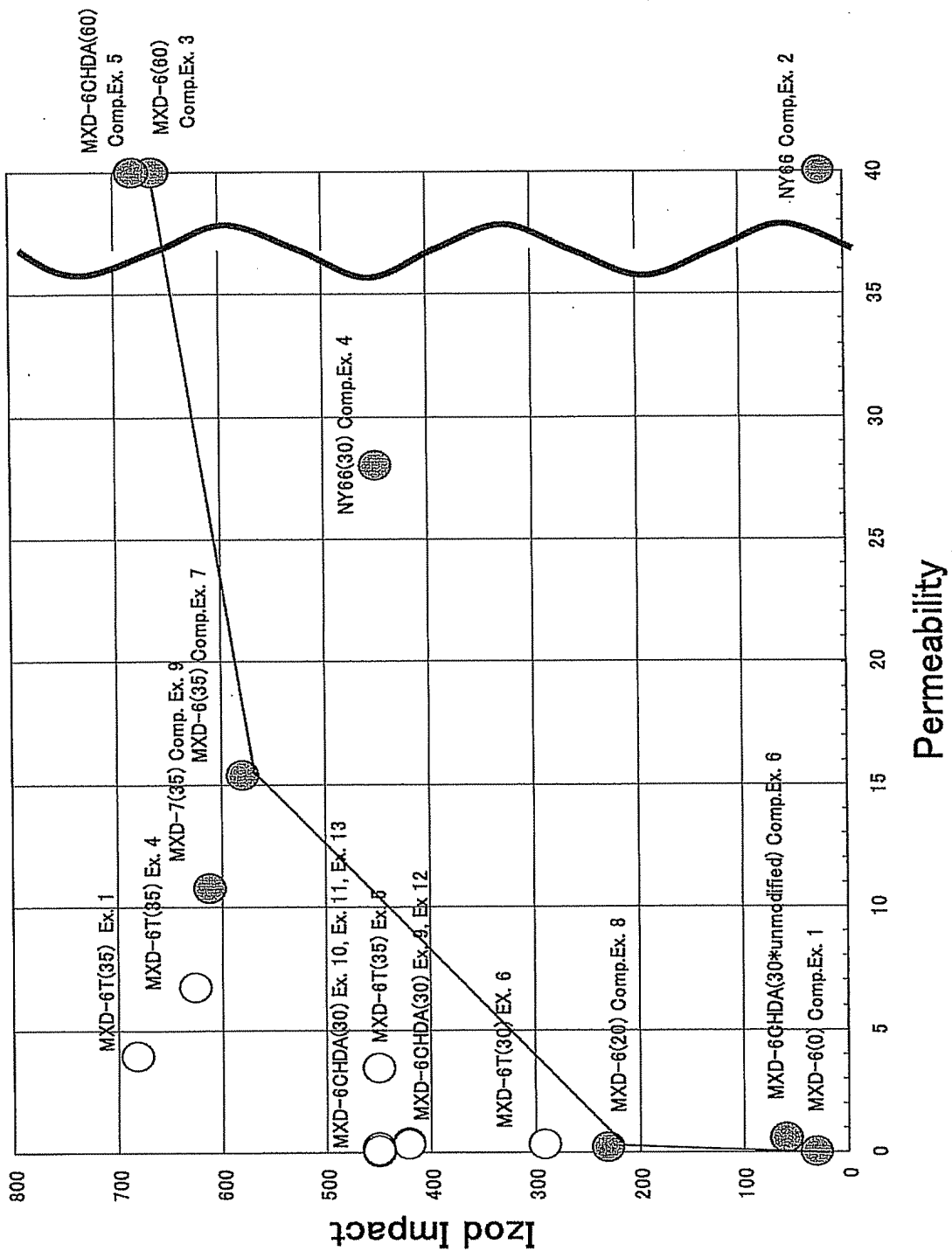
Table 5

		Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Composition	(1)MXD-6			
	(2)MXD-6T			
	(3)MXD-7			
	(4A)MXD-6CHDA-10A		100	
	(4B)MXD-6CHDA-10B			100
	(5A)MXD-6CHDA-20A			
	(5B)MXD-6CHDA-20B			
	(6)nylon 66	100		
	(i)modified L-MDPE			
	(ii)modified copolymer	43	150	
Properties	(iii)modified copolymer			
	(iv)unmodified copolymer			43
	tensile strength (MPa)	39	9	35
	tensile elongation (%)	>160	>160	15
	tensile elastic modulus (GPa)	1.6	0.3	1.9
	izod impact strength (J/m) at -40°C	450 - NB	NB	60
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	28	680	0.60
	morphology structure	A	B	A
	average particle diameter (μm) of domain	0.8	-	80

Table 6

		Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9
Composition	(1)MXD-6	100	100	
	(2)MXD-6T			
	(3)MXD-7			100
	(4A)MXD-6CHDA-10A			
	(4B)MXD-6CHDA-10B			
	(5A)MXD-6CHDA-20A			
	(5B)MXD-6CHDA-20B			
	(6)nylon 66			
	(i)modified L-MDPE			
	(ii)modified copolymer	54	27	54
	(iii)modified copolymer			
	(iv)unmodified copolymer			
Properties	tensile strength (MPa)	39	44	35
	tensile elongation (%)	>160	>160	>160
	tensile elastic modulus (GPa)	1.6	2.0	1.5
	ized impact strength (J/m) at -40°C	580	230	610
	alcohol-containing gasoline barrier property (g·mm/m <sup>2</sup> ·day)	15.4	0.25	10.8
	morphology structure	A	A	A
	average particle diameter (μm) of domain	0.7	0.8	0.9

FIG. 1



As is clear from the above-mentioned results, in Examples 1, 4 - 6, 9 - 13 of the present invention, Izod Impact was high and Permeability was low (Fig. 1). Hence, it has been demonstrated that the materials of the present invention are superior in the relationship between the both properties of impact strength at a low temperature of -40°C and alcohol-containing gasoline barrier property.

The materials of Examples 1, 4 - 6, 9 - 13 comprise a polyamide resin as a matrix component, and a polyolefin resin finely dispersed therein as a domain having an average particle diameter of 0.5 - 1.5  $\mu\text{m}$ .

In Comparative Example 6, the average particle diameter of the domain became very large presumably because the polyolefin resin did not have a functional group capable of reacting with polyamide resin (A) and the both resins did not react with each other.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed at *Fuku*, Japan on this 23 day of April, 2008

..... *Gaku Maruyama* .....

Gaku MARUYAMA